

The Infra-Red Bands of Hydrogen Peroxide at $\lambda 9720$ and the Structure and Torsional Oscillation of Hydrogen Peroxide

LLOYD R. ZUMWALT* AND PAUL A. GIGUÈRE†

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

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A high dispersion study of the OH bands of hydrogen peroxide in the photographic infra-red is described. The rotational structure of the two hybrid bands at $10,283.68\text{ cm}^{-1}$ and $10,291.08\text{ cm}^{-1}$ is analyzed. The small moment of inertia of hydrogen peroxide is found to be $2.78_6 \times 10^{-40}\text{ g cm}^2$ while the harmonic mean of the two larger moments of inertia is found to be approximately $33.9 \times 10^{-40}\text{ g cm}^2$. The planar *cis*-configuration is ruled out spectroscopically and it is concluded that hydrogen peroxide exists in a non-planar form. It is tentatively decided that the vibrational levels of hydrogen peroxide are doubled and that the double minimum potential associated with the internal rotation of the OH groups has a high and a low barrier.

INTRODUCTION

THE position of the OH groups with respect to their relative rotation about the O—O bond in hydrogen peroxide is of some interest. The OH groups can be imagined as preferring to assume the planar *cis*- or *trans*-configurations or some intermediate non-planar configuration. In the third case the molecule will have two equivalent enantiomorphous forms and the hindering potential for internal rotation will have two minima of equal depth and, in general, two barriers of unequal height. The OH groups undergo free rotation, hindered rotation or torsional oscillation depending on the heights of the barriers of the hindering potential.

Penney and Sutherland¹ have proposed a non-planar structure for hydrogen peroxide where the azimuthal angle² is 100° . Both barriers are given as being fairly high. These deductions are based on theoretical considerations and are shown to give a calculated value of the electric moment which agrees well with that obtained from measurements of the dielectric constants of dilute solutions of hydrogen peroxide in dioxane.³

Evidence of hindered rotation or torsional oscillation should appear in the rotational fine structure of the infra-red bands. In the hope of obtaining such evidence we have recently studied

the absorption spectrum of hydrogen peroxide vapor in the photographic infra-red. The result has been the discovery of an unusual pair of bands at $\lambda 9720$ which give some information regarding the structure and torsional motion of hydrogen peroxide.

EXPERIMENTAL

The hydrogen peroxide used in these experiments had a strength which ranged from 95 to 98 percent. It was prepared from the commercial 30 percent solution by distillation under reduced pressure. The absorption cell was a six-meter Pyrex tube (22 mm diam.) which was heated to 100°C and through which hydrogen peroxide was continuously distilled at a pressure of 90 mm. Hydrogen peroxide which had been carefully purified was found to decompose very little on boiling. It was important to keep the all-Pyrex system very clean. Contact of the vapor with dirt or even a rough spot on the glass was found to cause violent decomposition.

When a tungsten lamp was used as a light source, the exposure time required for the high dispersion spectrogram was found to be excessive, consequently a carbon arc was employed as a light source. It was found necessary to run the carbon arc in an atmosphere of carbon dioxide to eliminate emission lines of the red CN bands. This light source reduced the required time of exposure by a factor of four; thus the spectroscopic plate was amply exposed in eight hours. During this time approximately two liters of the concentrated hydrogen peroxide were dis-

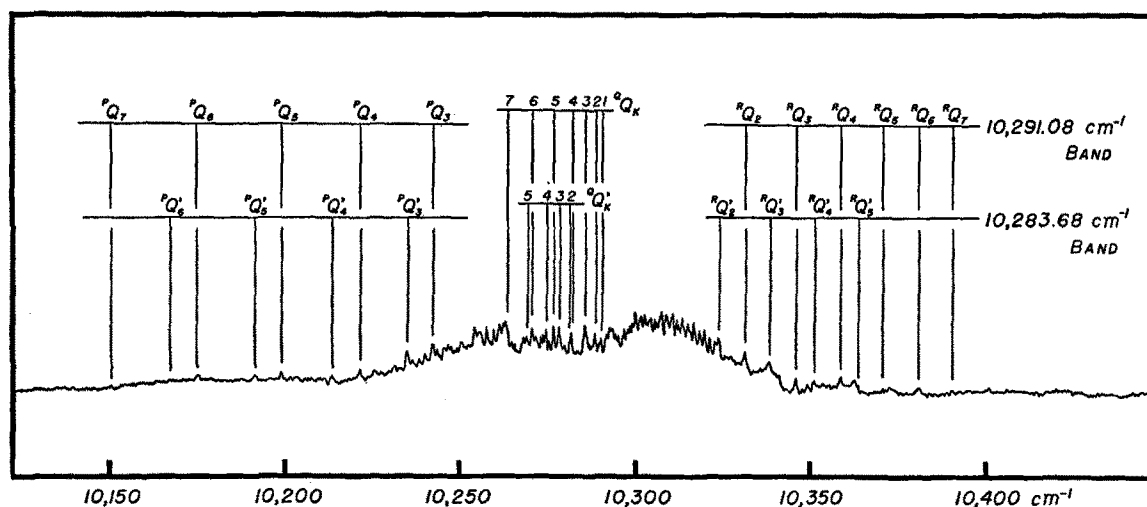
* Arthur A. Noyes Fellow in Chemistry.

† Provincial Government of Quebec Fellow in Chemistry.

¹ W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.* **2**, 492 (1934).

² The angle between the OH groups as seen projected on a plane normal to the O—O bond.

³ E. P. Linton and O. Maass, *Can. J. Research* **7**, 81 (1932).

FIG. 1. Microphotometer trace of hydrogen peroxide bands at $\lambda 9720$.

tilled over. The decomposition was only about 2 percent.

Exploration spectrograms were taken on Eastman 1Z plates with a glass Littrow spectrograph which covered the region between 7500 and 12,000Å. Only one band at 9720Å was found and this was then photographed in the first order of a twenty-one-foot concave grating spectrograph using Eastman 144Q plates. Measurements of the high dispersion plates were made with reference to third-order iron arc lines.

Rotational structure of band

An examination of the high dispersion spectrogram shows that a hybrid band is present which has the Q branches characteristic of both the parallel and the perpendicular bands of a symmetrical rotator molecule. The appearance of this band is analogous to that of the 10,477Å band of hydrazoic acid.⁴ In the case of hydrogen peroxide, as in the case of hydrazoic acid, there is a strong dependence of the small moment of inertia upon the vibrational state, thus the parallel sub-bands are separated and an unusually marked convergence is present in the perpendicular component. A second hybrid band occurring at a slightly lower frequency also appears. This band is similar to the first but is a little less intense. The Q_K branches⁵ of the

parallel component and the PQ_K and RQ_K branches of the perpendicular component of the two bands have been identified. The branches of the lower frequency band which occur at a displacement of 7.40 cm^{-1} have been given primed symbols.

A careful scrutiny reveals that at least a part of the band system appears to have a quadruplet character rather than a doublet character. Thus in the instances where $K''=3, 4, 5, 6$ a satellite of PQ_K' occurs at a shift of about minus 3.8 cm^{-1} and also a satellite of PQ_K occurs at a shift of about plus 3.8 cm^{-1} . These attendant lines are weak and somewhat difficult to measure; never-

TABLE 1. Frequency and identification of lines in the absorption spectrum of hydrogen peroxide at $\lambda 9720$.

IDENTIFICATION	FREQUENCY CM^{-1}	IDENTIFICATION	FREQUENCY CM^{-1}
PQ_7	10,151.49	Q_4'	10,274.76
a_6	164.69	Q_5	276.95
PQ_6'	168.21	Q_3'	278.55
PQ_6	175.94	Q_2'	281.39
b_6	179.65	Q_4	282.12
a_5	188.24	Q_3	286.06
PQ_5'	191.94	Q_2	288.82
PQ_5	199.25	Q_1	290.40
b_5	203.23	RQ_3'	339.21
a_4	210.28	RQ_3	346.51
PQ_4'	213.96	RQ_4'	351.86
PQ_4	221.49	RQ_4	359.56
b_4	225.51	RQ_5'	364.44
a_3	231.10	RQ_5	371.71
PQ_3'	235.06	RQ_6	382.27
PQ_3	242.41	RQ_7	391.82
Q_7	263.44		
Q_5'	269.37		
Q_6	270.72		

⁴ E. H. Eyster, J. Chem. Phys. 8, 135 (1940).

⁵ In this nomenclature the large letter describes the behavior of J in transition, the left-hand superscript gives the behavior of K , and the right-hand subscript gives the value of K in the lower state.

theless, they do seem to be real. The satellites have been named a_K and b_K , respectively. Corresponding branches are not seen on the high frequency side of the band centers.

Figure 1 gives a reproduction of the microphotometer trace of the grating spectrogram while Table I lists the frequencies⁶ and identifications of all lines which are assigned as Q branches and also of the satellites mentioned above.

It is to be noted that the PQ_2 , PQ_1 , RQ_0 and RQ_1 branches are not identified. There is no clear evidence of these branches although they are the strongest branches in the perpendicular band of the symmetrical rotator. This is probably due to the fact that the hydrogen peroxide molecule is a slightly asymmetric top and consequently the Q branches involving the levels where $K=0$ or 1 are considerably broadened. The QQ_1 branch involving transitions between levels where $K=1$, however, is observed. One, indeed, might expect the perpendicular band Q branches to be smeared out before the corresponding parallel band Q branches because in the limiting case of the symmetric rotator⁷ we know that the transitions involving the lowest J levels contribute most of the intensity to the latter branches while the higher levels contribute most of the intensity to the perpendicular band Q branches. When transitions between slightly perturbed levels of low J value are the principal contributors to the intensity of a Q branch then the branch is sharp and well defined. On the other hand when transitions between strongly perturbed levels of higher J value substantially contribute to a Q branch then the branch becomes greatly broadened and loses its identity.

The observed spectrum is characterized by multifold overlapping of sub-bands so that the fine structure is considerably confused and it is impossible to analyze the J structure of the sub-bands. Regular fine spacing is observed only on the high frequency side of the band centers. The fine spacing shows convergence towards high frequencies, and it falls off from 1.65 cm^{-1} to 1.59 cm^{-1} .

⁶ The frequencies are based on two independent sets of measurements on each of two high dispersion spectrograms.

⁷ See the expressions for the intensities of the branches of the symmetric rotator bands given by D. M. Dennison, Rev. Mod. Phys. 3, 313 (1931).

Analysis of band structure

The rotational energy of a symmetric rotator may be written:

$$F(J, K, v) = \sum_{ij} X_{ij}^v \{J(J+1)\}^i \{K^2\}^j. \quad (1)$$

The constant term X_{00}^v is omitted in the summation, and v represents the set of quantum numbers required to specify the vibrational state. The first coefficients are related to the effective moments of inertia as follows:

$$X_{01}^v = A_v - \frac{1}{2}(B_v + C_v), \quad X_{10}^v = \frac{1}{2}(B_v + C_v), \quad (2)$$

$$A_v = h/8\pi^2 c I_A^v, \quad B_v = h/8\pi^2 c I_B^v, \quad (3)$$

$$C_v = h/8\pi^2 c I_C^v, \quad A_v \gg B_v = C_v.$$

Hydrogen peroxide seems to be a slightly asymmetric rotator with B_v almost equal to C_v so that Eq. (1) very closely represents the characteristic energy values of the rotating molecule.

The constants X_{01}^0 and X_{02}^0 are evaluated by employing the following relations:

$$\frac{\Delta F''(K)}{2K+1} = X_{01}^0 + 2X_{02}^0 M + \dots; \quad M = (K + \frac{1}{2})^2 + \frac{1}{4}$$

and

$$\frac{\Delta_2 F''(K)}{4K} = X_{01}^0 + 2X_{02}^0 M + \dots; \quad M = K^2 + 1,$$

where the term differences are given by:

$$\Delta F''(K) = {}^QQ_K - {}^PQ_{K+1} = {}^RQ_K - {}^QQ_{K+1}$$

and

$$\Delta_2 F''(K) = {}^RQ_{K-1} - {}^PQ_{K+1}.$$

The frequencies of the assigned lines were found to be compatible with the above relations within experimental error. The best values for the constants of the equations were found to be:

$$X_{01}^0 = 9.23_1 \text{ cm}^{-1}, \quad X_{02}^0 = -0.0008_5 \text{ cm}^{-1}.$$

Similarly the rotational constants for the excited state, which we will denote by $v=3$, were found to be:

$$X_{01}^3 = 8.66_8 \text{ cm}^{-1}, \quad X_{02}^3 = -0.0008_6 \text{ cm}^{-1}.$$

An identical treatment of the frequencies of the Q branches which are denoted by primed symbols gave rotational constants which, within

experimental error, were exactly the same as the above. The two hybrid bands thus seem to have precisely the same rotational structure.

Since it was impossible to analyze the J structure of the bands we were obliged to obtain an estimate of the rotational constant X_{10}^0 (which must be very nearly equal to X_{10}^3) from the regular fine spacing which is clearly resolved only on the high frequency side of the band centers. We took 1.65 cm^{-1} as the best average value of the fine spacing. This is related to the rotational constant as follows:

$$2X_{10}^0 \approx 1.65 \text{ cm}^{-1}$$

thus

$$X_{10}^0 \approx 0.825 \text{ cm}^{-1}.$$

We believe that the observed fine spacing arises from R branches of the parallel sub-bands. This being the case the convergence is such that the above estimated value of X_{10}^0 may be a little low.

The center of the band denoted by unprimed Q branches is given by:

$$G(3) - G(0) = {}^0Q_K + K^2(X_{01}^0 - X_{01}^3) + K^4(X_{02}^0 - X_{02}^3) + \dots$$

The best value for this was found to be $10,291.08 \text{ cm}^{-1}$. Similarly the center of the band denoted by primed Q branches was found to be $10,283.68 \text{ cm}^{-1}$.

The rotational constants $X_{01}^0 = 9.231 \text{ cm}^{-1}$ and $X_{10}^0 \approx 0.825 \text{ cm}^{-1}$ correspond, respectively, to the values of $I_A^0 = 2.786 \times 10^{-40} \text{ g cm}^2$ for the small moment of inertia and $2I_B^0 I_C^0 / (I_B^0 + I_C^0) \approx 33.9 \times 10^{-40} \text{ g cm}^2$ for the harmonic mean of the two larger moments of inertia of hydrogen peroxide.

Structure of hydrogen peroxide

The harmonic mean of the two larger moments of inertia is principally dependent on the length of the O—O bond in hydrogen peroxide. Calculation shows that the value given above corresponds to an O—O distance of about 1.48\AA .

The fact that the observed bands are of the hybrid type shows that the OH groups of hydrogen peroxide are not in the planar *cis*-configuration. If these groups were so situated, the molecule would have a point group symmetry C_{2v} and one would only observe pure perpen-

dicular or parallel type bands. Incidentally, we also know that the OH stretching vibration involved in the observed bands is antisymmetric. A symmetric stretching frequency would give a pure perpendicular band.

As shown by Linton and Maass³ the hydrogen peroxide molecule has a fairly large electric dipole moment. This rules out the *trans*-configuration and, thus, since the *cis*-form is ruled out spectroscopically, the hydrogen peroxide molecule must have a non-planar structure.

We are unable to give an estimate of the azimuthal angle² of the OH groups from our spectroscopic data although it appears that this angle cannot be between 85° and 95° . We conclude this because the absence of the PQ_2 , PQ_1 , RQ_0 and RQ_1 branches indicates the molecule is actually an asymmetric top while a calculation of the moments of inertia shows that a hydrogen peroxide molecule with an azimuthal angle of around 90° is not significantly asymmetric.

It is interesting to note that Lu, Hughes and Giguère⁸ in their recent x-ray studies of the "hyperol" crystal in these laboratories have found the hydrogen peroxide molecule to have an azimuthal angle of about 106° .

Discussion of the band structure

The bands which have been described and analyzed correspond closely to the type of band which is characteristic of a spindle-shaped symmetrical top molecule that is fairly rigid. The complete rotation of the OH groups about the O—O bond in hydrogen peroxide must be strongly hindered. A very different band structure would appear if there were a free or a weakly hindered internal rotation. In this case the band would have a more extended structure, a larger Q spacing and, in the event of a weakly hindered rotation, an irregular Q spacing.

The occurrence of two hybrid bands separated by 7.40 cm^{-1} must be explained. A visual examination of the spectrogram and the microphotometer trace shows that the low frequency band must be more than one-half as intense as the other band. The PQ_6 and ${}^PQ_6'$ branches which

⁸ Chia-Si Lu, E. W. Hughes, and P. A. Giguère, "Crystal structure of the urea-hydrogen peroxide addition compound, $\text{CO}(\text{NH}_2) \cdot \text{H}_2\text{O}_2$," to be published in J. Am. Chem. Soc.

occur where the background absorption is weak seem to have just about the same intensity. Assuming relative intensities of the *Q* branches are given by the matrix elements of the electric moment for the symmetric rotator given by Dennison,⁷ we calculate that the perpendicular component of the low frequency band is about two-thirds as intense as the same component of the other band.

Three possible explanations for the hybrid bands occur to us. The two bands may be thought to originate from two entirely different vibrational transitions. As they both have to be antisymmetric OH stretching frequencies, one might be the third harmonic of the antisymmetric frequency, and the other the combination frequency of the antisymmetric stretching frequency and the second harmonic of the symmetric stretching frequency. This explanation seems improbable, however, since the expected frequency difference is much larger than the observed doublet separation.

The two bands may be imagined to be members of a sequence of bands all of which involve the same vibrational transition but which involve absorption from different excited states. Thus the strongest band may originate in a transition from the ground state while the band displaced 7.40 cm^{-1} to lower frequencies originates in a vibrational transition that is different in that the torsion oscillation is excited in the lower and upper levels. In this case, however, there should appear a third member of the band sequence which is displaced about 7.40 cm^{-1} from the low frequency band and which is about two-thirds as strong as this band. Actually one is unable to discern a trace of a third member of the imagined band sequence; consequently we have decided that the two observed bands are not members of

a sequence of bands involving absorption from different excited states of the torsion vibration.

According to theory the vibrational levels of non-planar hydrogen peroxide are doubled. There will be a sizable doublet splitting if one of the barriers of the potential hindering the internal rotation of the OH groups is low. We are inclined to believe that this situation most plausibly accounts for the two bands of nearly equal intensity and identical rotational structure; hence we have tentatively decided that the bands arise from transitions between well-split doublet levels. The separation of 7.40 cm^{-1} of the observed bands probably represents the difference in the splitting of the ground state and the upper vibrational state. The doublet splitting which results from the double minimum and the one low barrier in the torsion potential may be expected to be different in the ground state from that in the excited vibrational state since there should be a rather strong interaction between the OH stretching motion and the torsional motion. Stretching of the OH bonds changes the moments of inertia of the torsionally oscillating OH groups and also changes the hindering potential.

At present we are unable to give an explanation of the apparent quadruplet character of part of the observed rotational structure.

In order that our decision concerning the origin of the bands may be confirmed a further spectroscopic study of hydrogen peroxide should be made. We hope to undertake soon the study of the fundamental bands and thereby obtain some additional information regarding the spectroscopic behavior and the nature of hydrogen peroxide.

In conclusion the authors would like to express their appreciation to Professor Richard M. Badger for his helpful advice and continued interest in this study.